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Observation of Propagation Speed of Conductive Front in Electrochemical Doping Process of Polypyrrole Films

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According to the propagation theory of a conductive zone for the electrochemical doping process of conducting polymer films, an oxidized conductive zone works as an electrode for oxidizing the reduced non-conductive region and is propagated throughout the film under charge transfer control. This theory was verified for polypyrrole films by tracing the temporal and spatial variations of conductive regions in a film. An exhaustively reduced polypyrrole film was laid on an insulating glass plate and connected electrically to an ITO electrode at the marginal part. The film absorbance to a monochromatic light beam was monitored with a photodiode array detector at 14 segments of the film. When the potential of the ITO electrode was stepped to an oxidation potential of the film, an electrochemically oxidized conductive zone was propagated through the film with a manifest phase boundary. The distance from the edge of the ITO electrode to the front of the conductive zone increased linearly with time. The logarithmic slope of the propagation speed exhibited a linear relation to the applied potential.

A conducting polymer film deposited on an electrode can be switched between a highly conductive oxidized (doped) state and a resistive (or insulating) reduced (undoped) state by controlling the electrode potential. This electrochemical conversion involves mass and charge transport in the film and heterogeneous charge transfer at the underlying electrode. Therefore, the composition of the film is non-uniform and varies with time during the process of conversion.

In order to predict the temporal and spatial variations in composition, we have proposed the propagation model of a conductive zone under charge transfer control.[1–4] This model is available when supporting electrolytes permeate sufficiently into the film and so mass transport of the supporting electrolyte does not limit the conversion rate. This model consists of the following processes: Initially the film is resistive or in the reduced state. When the potential of the underlying electrode was set more anodic than the oxidation potential of the film, first the film is oxidized only in a region very close to the underlying electrode and becomes locally conductive. This conductive region works as a new electrode for oxidizing the reduced non-conductive region on it. Then a reduced region very close to this new 'electrode' is subsequently oxidized and converted into the conductive to yield an additional new electrode. Through the repetition of this process, the conductive zone is propagated up to the top of the polymer film. The conversion rate is controlled by charge transfer at the interface between the conductive zone and the reduced region. This concept has been introduced by Lacroix and Diaz.[5]

We have verified this model for the electrochemical doping process of polypyrrole films by analyzing linear sweep voltammograms,[1] in situ spectroscopic voltammograms,[2] and chronoamperometric responses.[3] This model differs on the time dependence of current from the reported models; models for charge transport due to diffusion-like electron hopping[6–10] and due to both diffusion and migration,[11] a model analogous to a porous electrode which yields charging current,[12] a capacity model including deeply and shallowly trapped ions,[13] an RC time constant model,[14] and a film resistance model.[15]

An aspect of the propagation of the conductive zone can be seen from the temporal and spatial analysis of a distribution of conductive species in the film. In our previous paper,[4] a polypyrrole film was coated onto an addressable microband array electrode in the reduced state, and oxidized from the margin of the film by applying an oxidation potential only to the marginal electrode. The potentials of the other microband electrodes were expected to reflect the distribution of the conductive species on the basis of the Nernst equation. Unfortunately, these potentials were overlapped by the applied potential because the electrochemically generated conductive zone conducted the potential of the marginal electrode. In order to obtain the precise distribution of the conductive species, a non-electric measurement is required.

Polypyrrole shows great spectral change in visible and near-infrared regions with the conversion between the reduced and the oxidized states.[2,16] Therefore, the extent of oxidation or the concentration of the conductive species can be estimated from the absorbance at a wavelength at which it is sufficiently different between the two states. The distribution of such species which absorb the light with a particular wavelength can be measured with a photodiode array detector, a linear arrangement of small photodiode elements with a multichannel detector.[17,18] In this study, an exhaustively reduced polypyrrole film was laid on an insulating glass plate and connected electrically to an ITO electrode at the margin of the film. The film was oxidized by applying an oxidation potential to the ITO electrode, and variations in absorbance at 14 segments of the film were measured with the photodiode array detector. The relation between the distance from the ITO electrode to each segment and the time at which each absorbance begin to change gives the intuitive evidence of the propagation of the conductive zone.

Experimental

Chemicals. Pyrrole (Tokyo Kasei Ltd.) was distilled under reduced pressure (at 1.07×10^4 Pa) and stored in a sealed vessel at N_2 atmosphere. Acetonitrile was distilled successively with molecular sieves, 4A 1/16 (Wako, Tokyo), and with calcium hydride (Tokyo Kasei Ltd.) at N_2 atmosphere and stored in a sealed vessel at N_2 atmosphere. Lithium perchlorate anhydrous (Wako, Tokyo) was of analytical grade and was used as received.

Apparatus and Procedure. Polypyrrole was formed by applying a potential of 1.2 V (vs. SCE) to an ITO electrode (15 mm$\times$8 mm) for 40 s in an acetonitrile solution containing 0.06 mol dm^{-3} pyrrole, 0.1 mol dm^{-3} $LiClO_4$ and 1% H_2O at N_2 atmosphere at 25 °C. The ITO electrode was a glass plate coated on one side with In-Sn oxide (ITO) and supplied by ULCOAT (Saitama, Japan). The resistance of the electrode was 12 Ω cm^{-2}. A potentiostat was HA-301 (Hokuto Denko Ltd., Tokyo). Current vs. time curves for the polymerization were recorded with a *x*–*t* recorder, RW-21T (Rikadenki, Tokyo). The charge, Q, consumed in the polymerization was evaluated by integrating the current vs. time curve and was 0.133 C cm^{-2}. From the equivalence of 1 C cm^{-2} to 6.85 μm,[2] the film was 0.91 μm thick. The film was covered with a platinum plate so that is was sandwiched between the platinum and the ITO electrodes. The film was reduced exhaustively by applying a potential of −1.0 V (vs. SCE) to both the electrodes for 15 min in an N_2 saturated acetonitrile solution containing 0.1 mol dm^{-3} $LiClO_4$. Then the film turned uniformly yellow. Without the platinum plate, the film was not completely reduced and looked green. The reduced film was stripped

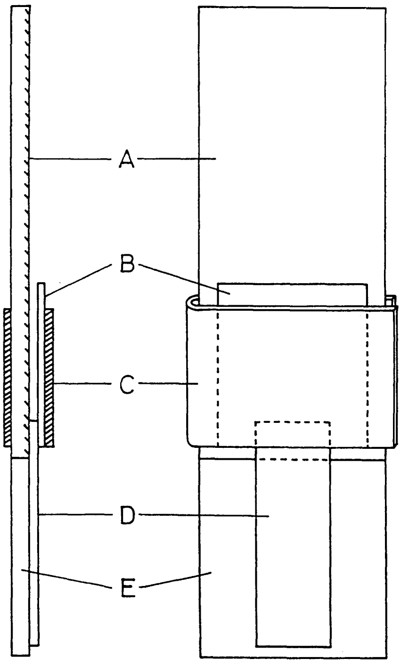

Fig. 1. Schematic diagram of the working electrode. (A) ITO electrode; (B) thin glass plate; (C) stainless steel holder; (D) polypyrrole film; (E) glass plate.

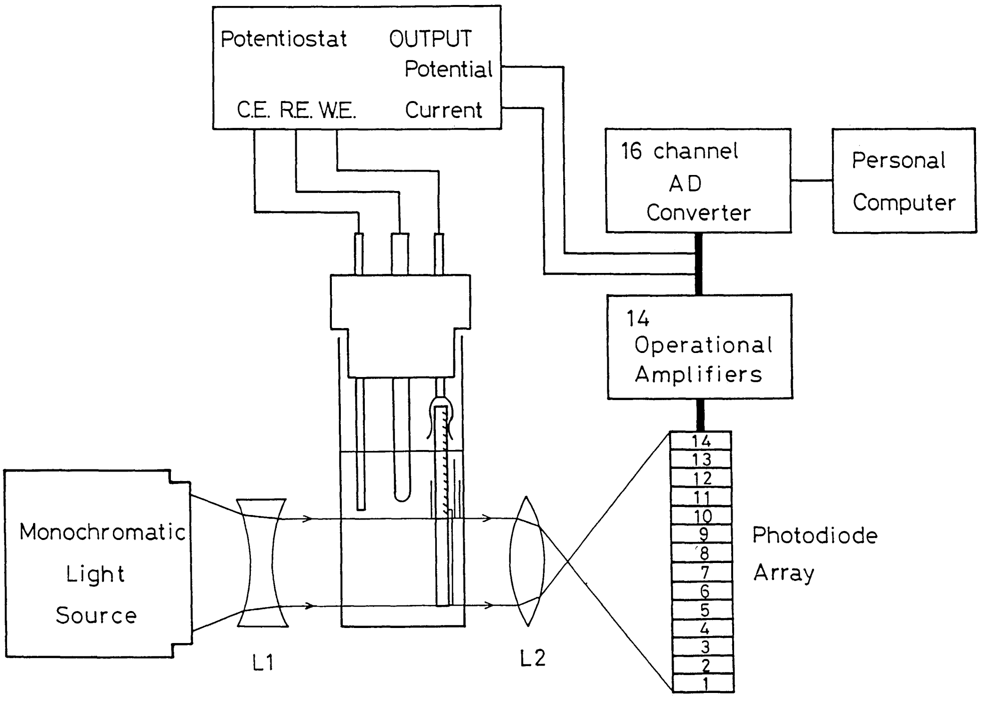

Fig. 2. Schematic diagram of optical apparatus. L1 is a concave lens (*f*=29 mm). L2 is a convex lens (*f*=28 mm).

from the ITO substrate and cut into a rectangle (6 mm×2 mm). It was laid on an insulating glass plate which was joined to an ITO electrode, so that the marginal part of the film (1 mm long) was on the ITO electrode (see Fig. 1). For electrical contact, the marginal part was pressed to the ITO electrode with a thin glass plate and a stainless steel holder. All these procedures were done at N_2 atmosphere in a glove box.

An optical apparatus is shown in Fig. 2. A rectangular (1 cm×1 cm) quartz cell with a teflon holder was used as an electrochemical cell. The top of the ITO electrode was clipped with a stainless steel holder so that the polypyrrole film was immersed into an N_2 saturated acetonitrile solution containing 0.1 mol dm^{-3} $LiClO_4$. A counter electrode was a platinum plate. A reference electrode was a saturated calomel electrode (SCE) which was connected to the electrochemical cell through a salt bridge filled with acetonitrile containing 0.1 mol dm^{-3} $LiClO_4$. Excitation light of a fluorescence spectrophotometer, Hitachi 650-40, was used as a monochromatic light source. A beam from the monochromatic light source was collimated with a concave lens L1 and passed through the polypyrrole film on the glass plate perpendicularly. The beam was then magnified by 2.8 times with a convex lens L2 and imaged onto 14 elements of a photodiode array, S2311-35Q (Hamamatu, Shizuoka, Japan), located on the image plane of the film. The photodiode elements were 0.94 mm wide and lined up at intervals of 0.05 mm. Since the image of the film was magnified by 2.8 times, the spatial resolution to the film was 0.36 mm. The 14 photodiode elements were connected to operational amplifiers through which photocurrent signals were converted to voltage signals. Deterioration in the spatial resolution by scattering of the excitation beam was negligible, which was confirmed by measuring the 14 photocurrents with attaching a narrow grid to the polymer film.

The polypyrrole film was oxidized by stepping the potential of the ITO electrode from −1.0 to 0.2 V (vs. SCE) or more anodic potentials. According to the result from the conductivity measurements of polypyrrole films reported by Feldman et al., polypyrrole is insulating at potentials more cathodic than −0.4 V (vs. SSCE) and highly conductive at potentials more anodic than 0.0 V.[19] Therefore, the films exhaustively reduced at −1.0 V (vs. SCE) and the films oxidized at 0.2 V or more anodic potentials can be considered as resistive and highly conductive, respectively. The stepped potential was limited up to the polymerization potential of the film, 1.2 V (vs. SCE), in order to avoid irreversible over-oxidation of the film which lead to the destruction of the polymer structure. The films oxidized at potentials between 0.2 V and 1.2 V (vs. SCE) could be reversed to the exhaustively reduced state by sandwiching the film between an ITO and a platinum electrodes and applying a potential of −1.0 V (vs. SCE) to both the electrodes.

After the potential of the ITO electrode was stepped, the 14 photocurrents measured with the photodiode array detector were recorded every 25 ms on a personal computer, PC-9801 (NEC, Tokyo), with potential and current outputs of the potentiostat through a 12 bits A/D converter, AZI-204 (Interface, Tokyo). Each photocurrent, i_p, was converted to the absorbance, A, at the corresponding segment of the film through the following equation:

$$A = -\log(i_p / i_p^\circ) \qquad (1)$$

where i_p° is the photocurrent measured without setting the film on the glass plate.

Absorption spectra of the polypyrrole film at various potentials were measured with a multichannel photodetector system, MCPD-1000 (Photal, Tokyo), sufficiently after the potential of the ITO electrode was stepped to each potential.

Time-sequence photographs were taken every 0.4 s with a single-lens reflex camera, Olympus OM-2, equipped with a lens, Zuiko Auto Macro 50 mm F3.5, and a motor-drive unit, Winder 2.

Results and Discussion

Figure 3 shows absorption spectra of the polypyrrole film in the exhaustively reduced state (at −1.0 V vs. SCE) and in the oxidized states (at 0.0, 0.4, and 0.8 V). The spectrum at −1.0 V showed a prominent absorption band centered at 420 nm. There was no peak at wavelengths longer than 500 nm, indicating that the film was in the completely reduced state. When the film was oxidized at 0.0 V, the band at 420 nm decreased and two broad bands appeared around 520 nm and in the near-infrared region (700—1000 nm). As the oxidation of the film proceeds (at 0.4 and 0.8 V), the band around 520 nm slightly decreased with shifting to the shorter wavelength and the band in the near-infrared region increased monotonically.

Figure 4 shows a chronoamperometric curve for the oxidation of the polypyrrole film when the potential of the ITO electrode was stepped from −1.0 to 0.8 V (vs. SCE). Immediately after the potential was stepped, large current flowed for a short period ($t<0.1$ s). After this pulsed current, the curve showed a plateau up to 5.8 s. Exhibition of the plateau is consistent with the theoretical chronoamperometric curve for a very rapid heterogeneous rate at the underlying electrode.[3] After showing the plateau, the curve decreased exponentially.

The absorbance vs. time curves simultaneously measured with the chronoamperometric curve (Fig. 4)

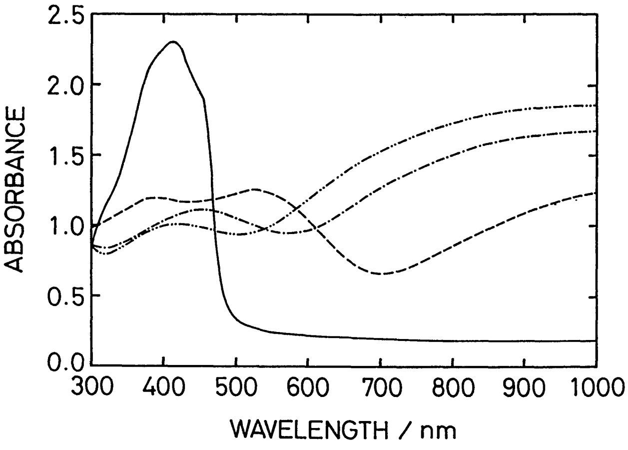

Fig. 3. Absorption spectra of a polypyrrole film at −1.0 (———), 0.0 (-----), 0.4 (-·-·-·-), and 0.8 V (vs. SCE) (-··-··-··-).

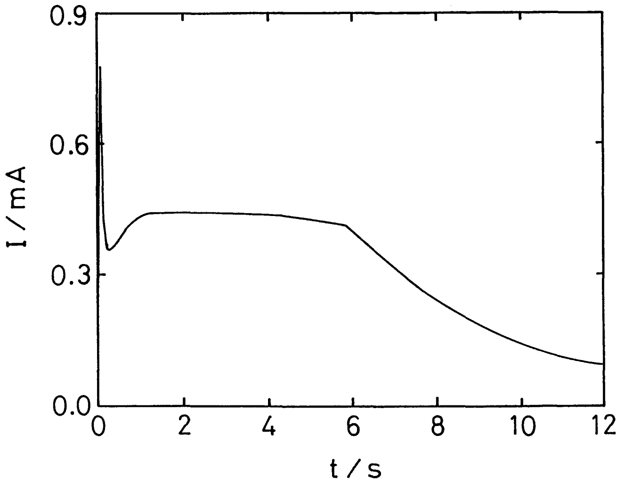

Fig. 4. Chronoamperometric curve of the polypyrrole film when the potential of the ITO electrode was stepped from −1.0 to 0.8 V (vs. SCE).

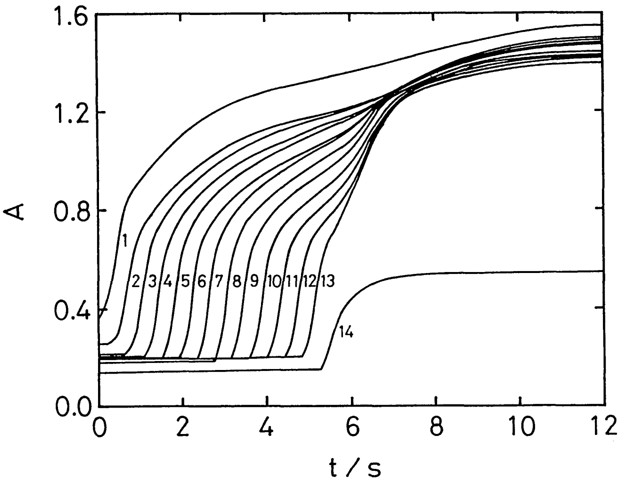

Fig. 5. Variations in the absorbance at 800 nm with time. The number marked beside the curves corresponds to the number of the photodiode element in Fig. 2.

are shown in Fig. 5. The monitored wavelength was 800 nm. Curve 1 represents the absorbance at the segment closest to the ITO electrode, and curve 14 represents the furthest segment. The higher absorbance in curve 1 was caused by scattering of the excitation beam at the joint between the glass plate and the ITO electrode. The lower absorbance in curve 14 was due to a shortage in length of the film. The further from the ITO electrode the segment was, the slower the absorbance began to change, indicating that the conversion proceeded from the electrode/film interface towards the end of the film.

The amount of charge, q, evaluated by integrating the chronoamperometric curve in Fig. 4, was 40 mC cm^{-2}. The efficiency of the oxidation, q/Q, was 0.30, being much greater than the value, 0.17, calculated from the maximum doping level (0.33) of polypyrrole perchlorate on the assumption that both q and Q did not include non-faradaic components. This large q/Q value suggests that the chronoamperometric cuve includes large capacitive components as observed in ordinary potential step experiments.

The initial pulsed current (t<0.1 s) in Fig. 4 can be ascribed to a capacitive current at the interface between the ITO electrode and the reduced film. The other source of the capacitive current is the interface between the conductive zone and the solution or the reduced region in the film. The conductive zone can be considered as a series connection of a resistor, R, and a capacitor, C. When a potential is applied to such a series connection of R and C, the capacitive current shows an exponential decay according to the product, RC (RC time constant). As the conductive zone is propagated in the film, both R and C should increase because they are proportional to the length (amount) of the conductive zone. Unfortunately, these capacitive components have not been separated mathematically from the faradaic current.[3] When the chronoamperometric curve began to decrease from the plateau (t=5.8 s), the absorbance vs. time curve 14 (in Fig. 5) had passed a half of the transition, namely, the top of the oxidized zone had reached the end of the film. Thus, the decreasing portion of chronoamperometric curve is mainly attributed to the capacitive current with a large RC time constant rather than the faradaic current.

Every absorbance vs. time curve in Fig. 5 changed at two stages; a steep rise from the initial value (0.18—0.25 for curves 2—13) to the intermediate value (0.67—0.68) and the following gradual increase to the final steady state value (1.4—1.5). Absorbance vs. time curves at 400 nm showed a precipitous fall from the initial value to the final steady state value. At 550 nm, they showed a steep rise from the initial value to a intermediate value followed by a gradual decrease to the final steady-state value.

The change at two stages observed at 800 and 550 nm indicates the presence of an intermediate state between the exhaustively reduced state and the final oxidized state. The intermediate state in polypyrrole has been found by in situ spectroscopic voltammetry[2] and ESR measurements.[20—23] Simultaneous ESR and electrochemical measurements[21—23] have demonstrated the participation of polaron (radical cation) as an intermediate between the neutral form in the reduced state and bipolaron (dication) in the sufficiently oxidized state. Therefore, the intermediate state may correspond to the polaron, and the final oxidized state to the bipolaron. The intermediate state is not observed when the conversion from the intermediate to the final state is much faster than that from the initial to the intermediate state. Therefore, the conversion from the polaron to the bipolaron is considered to be slower than that from the neutral form to the polaron.

Both the regions in the intermediate state and in the final oxidized state can be considered as conductive because both polaron and bipolaron have been considered as conductive species.[23,24] Therefore, the rapid change in the absorbance vs. time curves from the initial value to the intermediate value indicates the presence of a distinctive conductive zone rather than a vague boundary as observed in diffusion. A diffusional process such as charge transfer by electron hopping or electron exchange in the film might provide more gradual change with an increase in distance from the ITO electrode.

Since the film absorbance increased monotonically with the extent of oxidation at a wavelength in the near-infrared region, we can estimate the concentration of oxidized species, C_O, (and reciprocally the concentration of reduced species, C_R,) from it. When it is assumed that $C_O=0$ in the exhaustively reduced state and $C_R=0$ in the final oxidized state, the ratio of C_O to C_O+C_R is estimated from the absorbance, A, through the following equation:

$$C_O/C^* = (A - A_0)/(A_\infty - A_0), \tag{2}$$

where $C^*=C_O+C_R$, A_0 is the absorbance in the exhaustively reduced state, and A_∞ is that in the final oxidized state. If we apply Eq. 2 to the result of the spatially resolved spectral measurement, we obtain concentration vs. distance profiles of the oxidized species in the film.

Figure 6 shows the concentration vs. distance profiles of the oxidized species in the film at various times calculated from the absorbance vs. time curves in Fig. 5. A representative distance from the ITO electrode to the each monitored segment is the distance, d, from the edge of the ITO electrode to the center of the each segment. The small circles in Fig. 6 represent the center of the 14 monitored segments of the film. Both C_O/C^* at a given d and d at a given C_O/C^* increased with time. These concentration profiles are similar to the theoretical ones derived from the propagation theory.[3] Since the intermediate state, at which $A=0.67$—0.68 for curves 2—13 in Fig. 5, corresponds to $C_O/C^*=0.37$, the segment in which $C_O/C^*>0.37$ can be considered as the conductive region. Therefore, the steep concentration gradients below $C_O/C^*=0.37$ indicate the presence of a manifest phase boundary between the conductive zone and the resistive region.

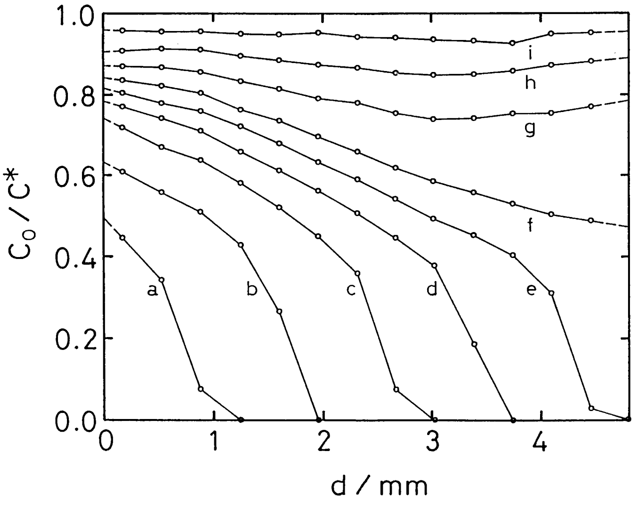

Fig. 6. Concentration vs. distance profiles of the oxidized species in the film at t=(a) 1.0, (b) 2.0, (c) 3.0, (d) 4.0, (e) 5.0, (f) 6.0, (g) 7.0, (h) 8.0, (i) 10.0 s. Dashed lines represents the extrapolation.

Figure 6 obviously shows that the conversion proceeded from the electrode/film interface towards the end of the film. For conducting polymer films deposited on ordinary solid electrodes, the relation between the rate-limiting process and the conversion direction has been considered as follows: When the conversion rate is limited by charge transfer in the film, the conversion occurs from the electrode/film interface towards the solution/film interface:[25] When the conversion rate is limited by mass transport of supporting electrolytes in the film, the conversion occurs in the reverse direction.[26] In our experimental condition, the direction of the ion transport is perpendicular to the direction of the film length. Therefore, if conversion proceeded with the mass transport being the rate-limiting process, the conversion has occurred from the upper layer of the film and seemed to occur from the whole of the film without depending on the distance from the electrode. Therefore, the conversion from the electrode/film interface indicates that the conversion proceeded with the charge transfer being the rate-limiting process.

In some previous papers, however, conversion with the mass transport being the rate-limiting process has been reported for polypyrrole films.[26-29] The reason why different rate-limiting processes have been observed for the same kind of polymer film may be attributed to the difference in permeability and porosity of the film which effects mobility of dopant ions in the film. Slow conversion from the fringe (solution/film interface) was also observed in our experimental condition when the film was sandwiched with two glass plates, in which the supporting electrolyte was supplied only by capillary action through the gap between the two glass plates and so the conversion might occur with the mass transport being the rate-limiting process.

The distance, d_{CF}, from the edge of the ITO electrode to the front of the conductive zone is an intercept of the abscissa in the concentration vs. distance profiles. However, they sometimes deviate from the real profiles especially at the conductive front, because the 14 measuring points is insufficient to describe the steep concentration gradient at the conductive front. Consequently, curves a, c, and d in Fig. 6 seemed to lean back in $C_O/C^*<0.1$. Therefore, the d_{CF} was estimated approximately with d at $C_O/C^*=0.1$. In Fig. 7, the d_{CF} was plotted against t at various stepped potentials, E's.

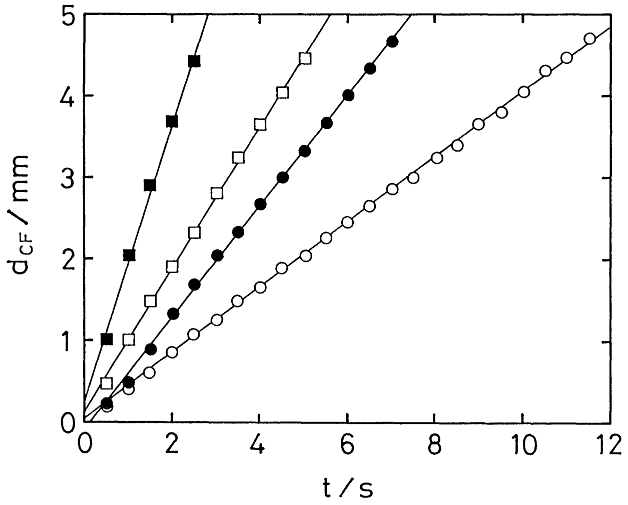

Fig. 7. Plots of $d_{\rm CF}$ against t at E=(○) 0.2, (●) 0.4, (□) 0.8, and (■) 1.2 V (vs. SCE).

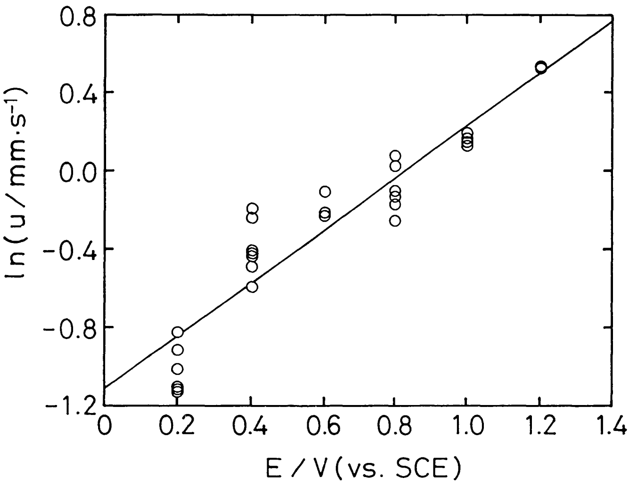

Fig. 8. Dependence of u on E. Values of u are the slope in Fig. 7.

These plots fell on the each straight line, indicating that the conductive zone was propagated in the film at a constant speed according to the applied potential. The propagation speed, u, is the slope of each line. A typical speed was 1.0 mm s^{-1} at E=0.8 V (vs. SCE). The linear relation of $d_{\rm CF}$ with t has been predicted from the propagation theory of a conductive zone in which the charge transfer at the interface between the conductive zone and the resistive region being the rate-limiting process.[3] This linear relation does not support any diffusional charge transfer process such as charge transport by electron hopping or electron exchange in the film. In such diffusional process, $d_{\rm CF}$, which corresponds to the thickness of the diffusion layer, should have increased with $\sqrt{t}$.

The logarithm of the propagation speed (u) was plotted against E in Fig. 8. They exhibit a linear relation, i.e. the propagation speed varies exponentially with the applied potential. This exponential relation indicates that the propagation is controlled by a charge transfer process of the Tafel type.

An aspect of the propagation could be seen in time-sequence photographs (Fig. 9) taken after the potential of the ITO electrode was stepped from −1.0 to 0.8 V (vs. SCE). Initially, the polypyrrole film was in the exhaustively reduced state and was uniformly yellow (Fig. 9a). After stepping the potential, the purple conductive zone grew, invading the yellow reduced domain (Figs. 9b and c). The distinctive phase boundary does not support the diffusive propagation but suggests the propagation under the charge transfer control as at a conventional electrode/solution interface. The distinctness of the boundary was independent of applied potentials in the range from 0.2 to 1.2 V (vs. SCE). It has been reported that a rapid charge transfer rate makes the boundary vague.[30] Thus the rate constant belongs to the totally irreversible case.[30] The purple zone was followed by a blue-black zone with a vague phase boundary (Figs. 9 c and d). The purple and

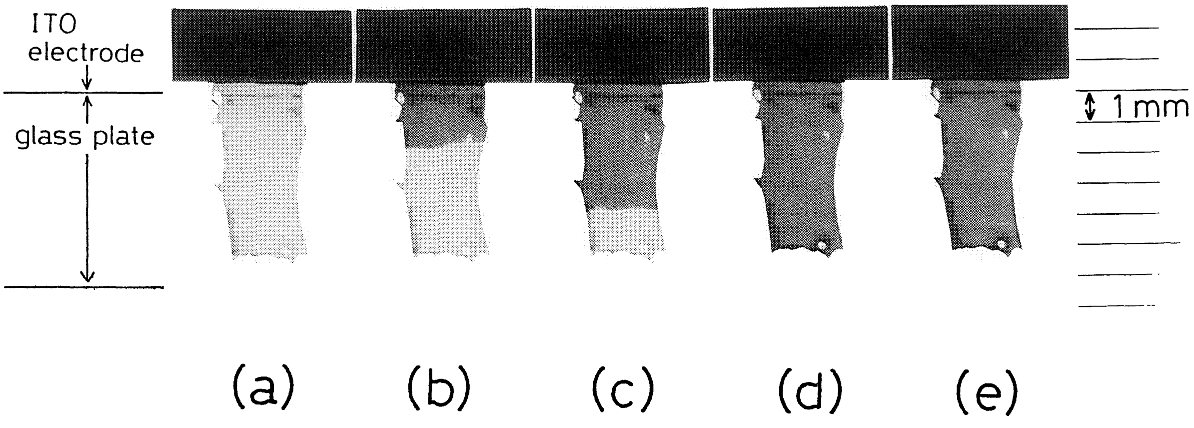

Fig. 9. Time-sequence photographs of a polypyrrole film at t=0 (a), 1.6 (b), 3.2 (c), 4.8 (d), 9.6 (e) s.

the blue-black zones were observed when the potential was more anodic than 0.2 V (vs. SCE). The film finally turned uniform in the blue-black state (Fig. 9 e).

Apparently, the purple zone corresponds to the intermediate state and the blue-black zone to the final oxidized state, therefore, they may correspond to the polaron and the bipolaron, respectively. The transient appearance of the intermediate state (polaron) is consistent with the transient ESR responses in polypyrrole films reported by Zhong et.al.,[23] in which the intensity of the ESR signal initially increased to a maximum and afterwards decreased to a steady state when the potential was stepped to 0.2 V (vs. SCE) or more anodic potentials.

In conclusion, the oxidation of resistive polypyrrole films obeyed the propagation theory of a conductive zone under charge transfer control in that (1) the distinctive phase boundary was observed; (2) the propagated distance was linear to the time of the electrolysis; (3) the propagation speed exhibited the exponential dependence on the applied potential.

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